



TITLE:

# <Division of Synthetic Chemistry>Organoelement Chemistry

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CITATION:

<Division of Synthetic Chemistry>Organoelement Chemistry. ICR Annual Report 2013, 20: 4-5

ISSUE DATE:

2013

URL:

<http://hdl.handle.net/2433/185266>

RIGHT:

# Division of Synthetic Chemistry – Organoelement Chemistry –

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## Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of “dreams” for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry.

### KEYWORDS

Steric Protection    Kinetic Stabilization    Low-coordinated Species  
Heteroatom    Transition Metal Complexes



## Selected Publications

Agou, T.; Nagata, K.; Tokitoh, N., Synthesis of a Dialumene-Benzene Adduct and Its Reactivity as a Synthetic Equivalent of a Dialumene, *Angew. Chem. Int. Ed.*, **52**, 10818-10821 (2013).

Agou, T.; Wasano, T.; Jin, P.; Nagase, S.; Tokitoh, N., Syntheses and Structures of an “Alumole” and Its Dianion, *Angew. Chem. Int. Ed.*, **52**, 10031-10034 (2013).

Sakagami, M.; Sasamori, T.; Sakai, H.; Furukawa, Y.; Tokitoh, N., 1,2-Bis(ferrocenyl)-Substituted Distibene and Dibismuthene: Sb=Sb and Bi=Bi Units as  $\pi$  Spacers between Two Ferrocenyl Units, *Chem. Asian J.*, **8**, 690-693 (2013).

Sasamori, T.; Tokitoh, N., A New Family of Multiple-Bond Compounds between Heavier Group 14 Elements, *Bull. Chem. Soc., Jpn.*, **86**, 1005-1021 (2013).

## Synthetic Equivalent of a Dialumene

Multiply bonded species involving heavier main-group elements have been extensively investigated, whereas the chemistry of analogous species involving group 13 elements is still in its infancy. Examples for isolable neutral heavier group 13 dimetallenes with the formula of  $R-M=M-R$  (M: Al, Ga, In, Tl) remain scarce for the homologues of gallium, indium, and thallium, and have been unknown for aluminum so far.

The dialumene-benzene adduct **1** was obtained by the reduction of the 1,2-dibromodialumane in benzene. The  $C_6H_6$  moiety of **1** was readily exchanged with  $C_6D_6$ , naphthalene, anthracene, and bis(trimethylsilyl)acetylene at room temperature, thus affording the corresponding trapping products of dialumene **2**. It was demonstrated that **1** shows unique reactivity as a synthetic equivalent of **2** for applications in the development of new organoaluminum species.

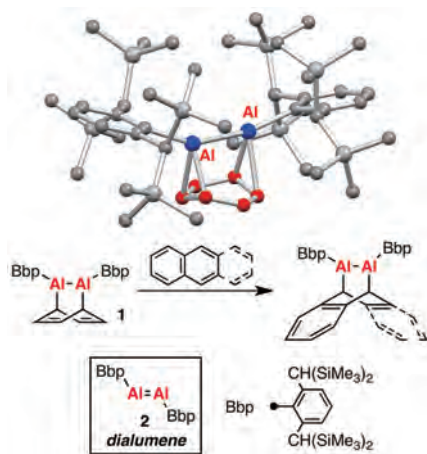


Figure 1. Structure and reactivity of dialumene-benzene adduct **1**.

## Alumole and Its Dianion

Heteroles of electron-deficient group 13 elements are expected to have low-lying LUMOs owing to the orbital interactions between the empty  $\pi$  orbital of group 13 elements and the  $\pi^*$  orbitals. To date, only a few examples of alumole (aluminacyclopentadienes)–Lewis base complexes have been structurally characterized. The coordination of Lewis bases to the aluminum center may substantially affect the electronic structures, therefore the synthesis of Lewis base-free alumoles has been desired to provide a basis for the elucidation of the intrinsic nature of alumoles.

We have succeeded in the synthesis of a Lewis base free alumole **3** by the introduction of bulky substituent,  $Mes^*$  group. The  $AlC_4$  ring of **3** exhibits the C–C bond alternation. Reduction of **3** with lithium afforded the lithium salt of the alumole dianion **4**. DFT calculations revealed that the  $3p(Al)-\pi^*$  conjugation effectively lowers

the LUMO energy level of the alumole and that coordination of two lithium cations to the alumole dianion is a key factor to keep the planar  $AlC_4$  ring structure.

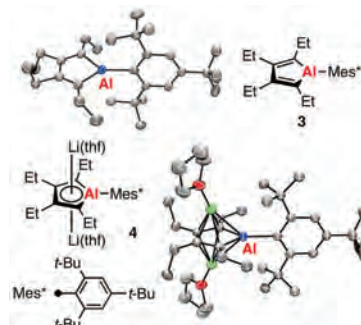


Figure 2. Structures of alumole **3** and its dianion **4**.

## 1,2-Bis(ferrocenyl)distibene and Dibismuthene

The d- $\pi$  electron conjugated systems consisting of bimetallic complexes with  $\pi$ -electron spacers,  $M-(\pi\text{-conjugated system})-M$  (M=transition metals), are extensively investigated from the viewpoint of their interesting electronic, optical, and magnetic properties.

We have succeeded in the synthesis of the first stable 1,2-bis(ferrocenyl)distibene **5** and 1,2-bis(ferrocenyl)-dibismuthene **6** by taking advantage of a newly developed bulky ferrocenyl group. The assessment of their structural parameters and physical properties indicated their definite  $Sb=Sb$  and  $Bi=Bi$  double-bond character. The electrochemical measurements revealed that distibene **5** and dibismuthene **6** exhibit stable, four-step (one reduction, three oxidation) redox processes reflecting the unique character of  $Sb=Sb$  and  $Bi=Bi$   $\pi$  bonds, and  $Sb=Sb$  and  $Bi=Bi$   $\pi$ -electron units can act as effective  $\pi$  spacers to couple with the two ferrocenyl moieties.

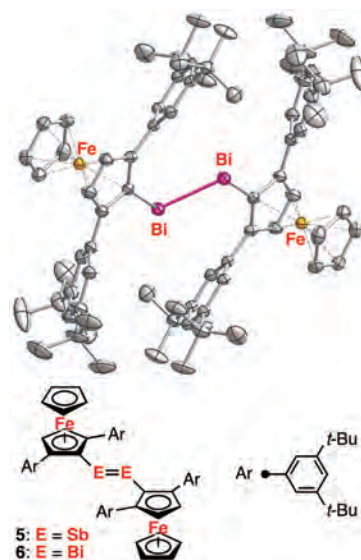


Figure 3. 1,2-Bis(ferrocenyl)distibene **5** and dibismuthene **6**.